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Experimental analysis of the grafting products of diethyl maleate onto linear and branched polyethylenes

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Abstract

This paper is focused on establishing the grafting products of diethylmaleate onto ethylene–α-olefin copolymers of varying comonomer contents. Several commercial ethylene/α-olefin copolymers ranging in comonomer contents from 0.35 to 3.70 mol% were used, as well as a hydrogenated polybutadiene (HPB) with a 1,2 unit content of 13.9 mol%. The polymers were functionalized with DEM in solution. The experimental techniques employed to verify the grafting and to ascertain the exact positioning of the insertion with respect to the branching points were: Fourier transform infra red spectroscopy (FTIR), carbon 13 nuclear magnetic resonance (^{13}C NMR) and Distortionless enhancement polarization transfer NMR (^{13}C NMR-DEPT). Thermal fractionation was performed by Differential Scanning Calorimetry (DSC) employing the successive self-nucleation and annealing technique (SSA).

The results obtained show that the DEM insertion onto polyethylene chains occurs in secondary carbons of the main chain regardless of the copolymer branch type and content. The reasons for this behavior may be related to a statistical factor being involved in the peroxide radical attack since there is an excess of secondary carbons as compared to tertiary ones per PE chain. Also, steric effects produced by the size of the DEM molecules are probably involved in the DEM insertion step. Our ^{13}C NMR-DEPT results suggest that DEM not only avoids the tertiary carbons where the branches are located but also, in polyethylenes with less than 4 mol% branch content, it prefers to insert in the secondary carbons that are at least 5 carbon atoms away from the branch point. In those cases where unsaturations are present in PE chain ends, FTIR shows that they can also be depleted by DEM grafting. However, in the HPB case where no unsaturations are present and the branching content is very high, the insertion still occurs only in the secondary carbons of the main chain. The thermal fractionation performed by SSA corroborated the aforementioned results since the fractions with the longest linear chains were always the first to be depleted by the grafting reactions. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Functionalization; ^{13}C NMR-DEPT; SSA

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1. Introduction

The modification of different types of polyolefins (polyethylene, PE; polypropylene, PP; ethylene–propylene copolymers, EPR) with polar groups has been studied by numerous authors [1–31]. Among these, the studies of Aglietto et al. [2,3] who have described the structure of the functional groups that are implanted onto high density polyethylene (HDPE) when the polymer undergoes a free radicals reaction in the presence of diethylmaleate (DEM) are noteworthy. These authors determined unequivocally, by means of the analysis of model molecules, that DEM is grafted to the HDPE as isolated units without homopolymerizing like in the case of other grafting agents such as maleic anhydride [3,21,22], acrylic acid [23] and some acrylates [24–26].

However, some fundamental aspects of the grafting mechanisms of the functionalization process are still unknown. Márquez et al. [18] have postulated recently, on the basis of thermal fractionation performed by differential scanning calorimetry (DSC), that the grafting of DEM onto linear low density polyethylene (LLDPE) in solution, occurs preferentially in the secondary carbons of LLDPE thereby interrupting the linear crystallizable sequences of the polymer. It has been argued [18] that the greater number

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Table 1
Molecular and structural characteristics of the samples employed in this work

Sample	M_w (g/mol)	M_w/M_n	Comonomer type	Comonomer content (mol%)	Density (g/cm^3)
HDPE1	175.000	9.4	1-Hexene	0.80	0.9465
HDPE2	144.000	6.2	1-Butene	0.35	0.9530
HDPE3	313.000	17.7	1-Butene	0.66	0.9493
HDPE4	222.000	12.3	1-Hexene	1.07	0.9433
LLDPE1	135.000	4.7	1-Butene	3.41	0.919
LLDPE2	150.000	4.3	1-Butene	3.70	0.9210
LLDPE3	–	–	4-Methyl-1-pentene		–
HPB	74.000	1.04	Ethyl branches	13.9	–

of secondary carbons in the LLDPE used as compared to tertiary ones favors the statistical grafting of DEM onto the secondary carbons. Furthermore, Ruggeri et al. [27] found for the functionalization of PE, EPR and PP, under the same conditions, that the final modification levels were in the following order: PE > EPR > PP. Similar results have been reported by Benedetti et al. [28] and Sipos et al. [17].

On the other hand, several researchers have previously reported [21,22,29–31] the functionalization of linear polyethylene in comparison with polyethylene copolymerized with different concentrations of α-olefins. According to these authors, the grafted monomer prefers to insert in the tertiary carbons or branching points rather than in the secondary carbons.

In previous works by Rojas and Fatou [14,19,32] the influence of the amount and type of branches in the function alization of PE with DEM in solution was studied. The results indicated that at least at the beginning of the grafting reaction, radical attacks on the terminal double bonds were preferred.

Recent developments of polyethylene synthesis have produced backbone chains with definite unsaturations, by means of the introduction of unsaturated cyclic comonomers [33]. The incorporation of such unsaturation in the PE chains makes them more reactive and adds interest to these systems.

In the present work, NMR and IR spectroscopy have been carried out on a set of ethylene copolymers with different types of α-olefin comonomers (1-butene, 1-hexene, 1-octene and 4-methyl-1-pentene), before and after grafting with DEM. Moreover, the polymers were analyzed by the application of successive self-nucleation and annealing (SSA), a new thermal fractionation technique developed by Müller et al. [18,34–39]. SSA is designed to produce molecular segregation during self-nucleation, crystallization and annealing produced by a complex thermal treatment using DSC. The main objective of this work is to identify the grafting products and on this basis formulate possible grafting reaction mechanisms as a function of the structural differences of the polyolefines under study.

2. Experimental

Commercial samples of copolymers of ethylene and several α-olefins were used for grafting, in addition to a hydrogenated polybutadiene (HPB) prepared in the laboratory. The commercial samples are denoted high and linear low density polyethylenes according to their density (HDPE and LLDPE, see Table 1). The HPB was obtained by anionic polymerization in cyclohexane, and then hydrogenated in homogeneous phase in the presence of a Titanocene complex [40]. The molecular size and constitutional characteristic of these polymers are given in Table 1.

The grafting reactions were carried out in solution using DEM in *o*-dichlorobenzene during 65 min at 160 °C in the case of the HDPE and 140 °C in the case of LLDPE and HPB. After grafting the samples were purified by soxhlet extraction, then they were dried 12 h at 60 °C. The initiator used was dimethyl-2,5-di-(*t*-butylperoxy)hexane (DBPH).

The grafting degree was measured by FTIR and ^{13}C NMR results using the calibration curves reported by us for such systems [14]. The grafting degrees are presented in Table 2.

^{13}C NMR spectra for the polymers under study were recorded using a 270 MHz Jeol Eclipse NMR spectrometer in 1,1,2,2-tetrachloroethane and in *o*-dichlorobenzene at 120 °C. Distortionless enhancement of NMR signals by polarization transfer (DEPT) was used in order to discriminate better the different types of carbons present in the polyolefines. In the samples of polyethylene before grafting, the ^{13}C NMR spectra allowed the determination of the type of comonomer present in the chain, following the assignments reported by De Pooter et al. [41].

Fig. 1 presents ^{13}C NMR spectrum of HDPE2 where the signal at 11 ppm evidences the presence of ethylene branches coming from the copolymerization of ethylene

Table 2
Amount of grafted diethylmaleate (DEM) in functionalized samples

Sample	Grafted DEM (mol%)	Grafted DEM (wt%)
HDPE1-*g*-DEM	2.08	12.8
HDPE2-*g*-DEM	1.59	9.77
HDPE3-*g*-DEM	1.36	8.35
HDPE4-*g*-DEM	1.73	10.6
LLDPE1-*g*-DEM	0.54	3.32
LLDPE2-*g*-DEM	1.50	9.21
LLDPE3-*g*-DEM	1.54	9.46
HPB-*g*-DEM	2.00	12.3

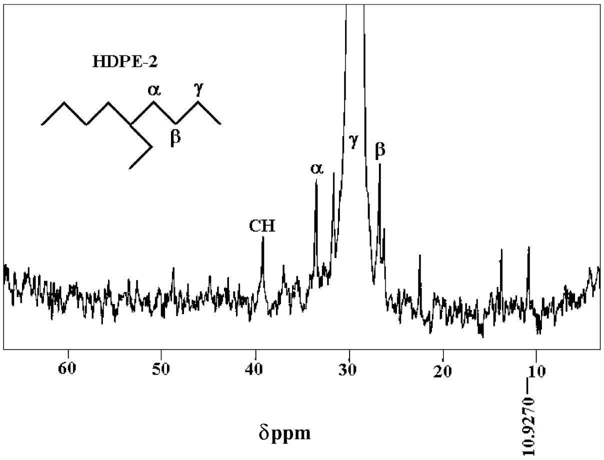

Fig. 1. ^{13}C NMR spectrum of HDPE2.

with 1-butene. Fig. 2, on the other hand, presents an example of a copolymer of ethyl and 1-hexene, in this case the signal at 13.7 ppm evidences the butyl branches present in the chain. The assignments for the bands observed are provided in the ^{13}C NMR spectra with the usual notation referred to the chemical structures shown in the inserts of Figs. 1 and 2.

Samples for FTIR were obtained by hot pressing films at 150 °C. The spectra were recorded on a Perkin Elmer spectrometer 16PC after 25 scans with a nominal resolution of 2 cm^{-1}.

For thermal analysis small discs were cut (10 mg) and encapsulated in aluminum pans. An inert atmosphere of nitrogen was used for all tests in a Perkin Elmer DSC7. The successive self-nucleation and annealing technique (SSA) was applied as follows [35]. The sample was first melted at 170 °C for 3 min. Then, it was cooled at 10 °C/min down to 25 °C in order to create an initial 'standard' thermal history. Subsequently, a heating scan at 10 °C/min was performed up to selected self-seeding and annealing temperature denoted T_s, where the sample was isothermally kept for 5 min before cooling it again at 10 °C/min down to 25 °C. Then the sample was heated in the DSC once more at 10 °C/min but this time up to T_s, which was 5 °C lower than the previous T_s and again held at this temperature for 5 min before cooling to 25 °C at 10 °C/min. This procedure is repeated, while T_s is being lowered at 5 °C intervals with respect to the previous step. The chosen T_s range was 139.5–69.5 °C. Finally, the melting behavior of the sample was recorded when the thermal conditioning was over. More details can be found in Refs. [34,35].

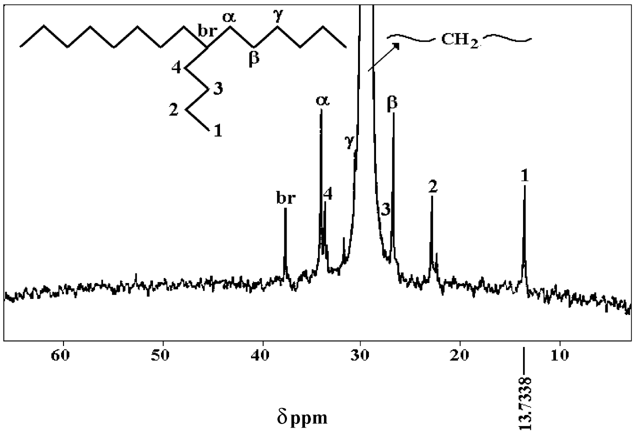

Fig. 2. ^{13}C NMR spectrum of HDPE1.

3. Results and discussion

3.1. NMR and IR characterization

The hydrogenated polybutadiene was compared with the ethylene/α-olefin copolymers because the HPB has a similar structure to a polyethylene copolymer with ethyl branches, but without unsaturations at chain ends. The absence of such unsaturations was verified by means of ^{13}C NMR as shown in Fig. 3. In that NMR spectrum, the absence of signals at 110–120 ppm, where the resonance of olefinic carbons is manifested, can be appreciated.

FTIR spectra were also consistent with the absence of terminal double bonds in the HPB. Fig. 4 shows two FTIR spectra of HPB and HPB-*g*-DEM, where it can clearly be seen that no bands attributable to chain ends double bonds in the polymer are present (these would be located at around 908 cm^{-1}). The bands present at 965.9 cm^{-1} in Fig. 4 are due to *trans* in chain unsaturations that are characteristic of residual 1,4 PB double bonds that were not hydrogenated.

On the other hand, the presence of chain ends unsaturations in commercial PE samples was detected in the FTIR spectra in the bands located at 908 and 920 cm^{-1}, which are the characteristic vibrations of vinyl end groups. FTIR spectra for three neat LLDPE polymers are presented as examples in Fig. 5 where bands at 908, 910 and 920 cm^{-1} can be clearly seen. Chain ends unsaturations were found in

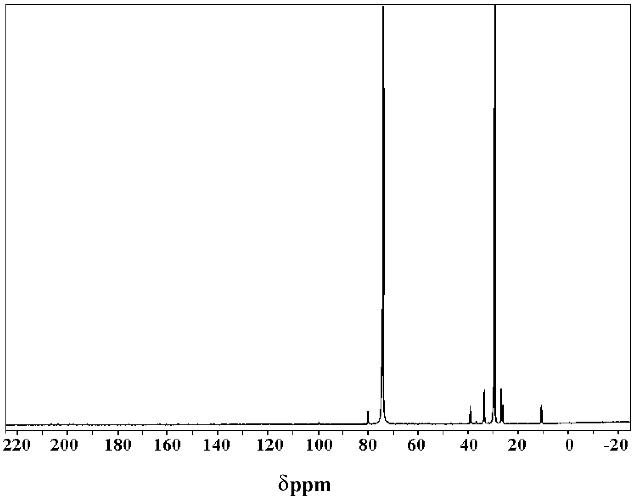

Fig. 3. ^{13}C NMR spectrum of HPB.

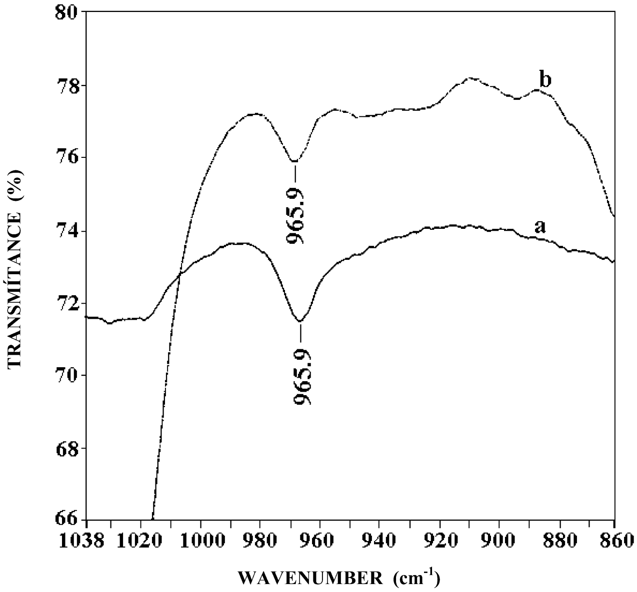

Fig. 4. FTIR spectra of: (a) HPB and (b) HPB-*g*-DEM.

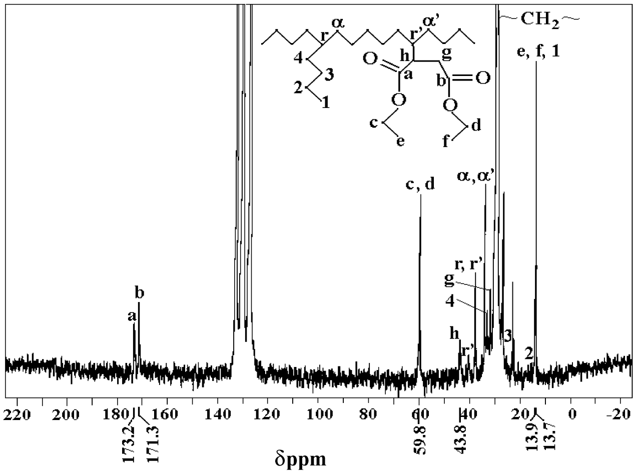

Fig. 6. ^{13}C NMR spectrum of HDPE1-*g*-DEM.

all the materials employed here with the exception of the HPB as mentioned above.

All ^{13}C NMR spectra obtained for the commercial polyethylene copolymers after grafting evidenced the introduction of DEM in the PE chains. In the ^{13}C NMR spectrum of Fig. 6 peak assignments are given that correspond to the microstructure of HDPE1-*g*-DEM. These assignments were made in agreement with the models reported by Aglietto et al. [2]. In Fig. 6, the new signals at 44 ppm and at 60 ppm correspond to the new groups inserted in the polyethylene chain (as compared to the unfunctionalized sample, Fig. 2). Particularly in this sample, the signal at 14 ppm not only indicates the presence of the CH_3 in the α-olefin branches (labeled 1), but also the CH_3 that are present in the grafted DEM (labeled e and f). The signals at 171 and 173 ppm are also characteristic of the grafted functional groups and constitute additional evidence of the successful modification carried out on the PE chain.

In addition to the ^{13}C NMR verification of the grafting reaction, the FTIR spectra of the commercial polyethylene copolymers obtained before and after functionalization indicate that the band located at 908 cm^{-1}, which corresponds to the vibrations of the unsaturations located at chain ends, shows a tendency to disappear upon grafting. An example is provided in Fig. 7 with FTIR spectra of HDPE4 before and after grafting, where it is evident that the band at 908.9 cm^{-1} suffers a great reduction in intensity upon grafting with DEM.

The application of the ^{13}C NMR-DEPT technique [42]

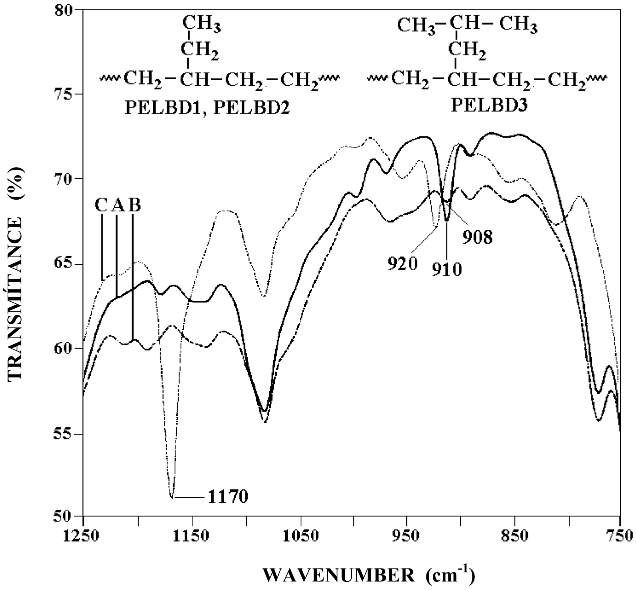

Fig. 5. FTIR spectra in the range 1250–750 cm^{-1} of: (a) LLDPE1, (b) LLDPE2 and (c) LLDPE3.

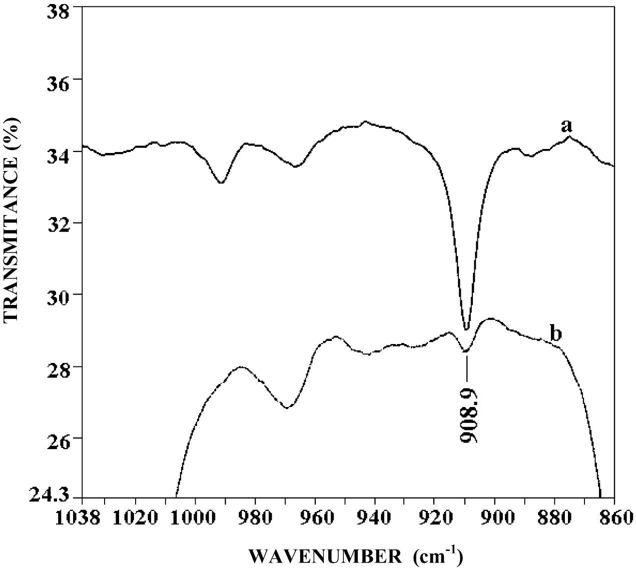

Fig. 7. FTIR spectra of: (a) HDPE4 and (b) HDPE4-*g*-DEM.

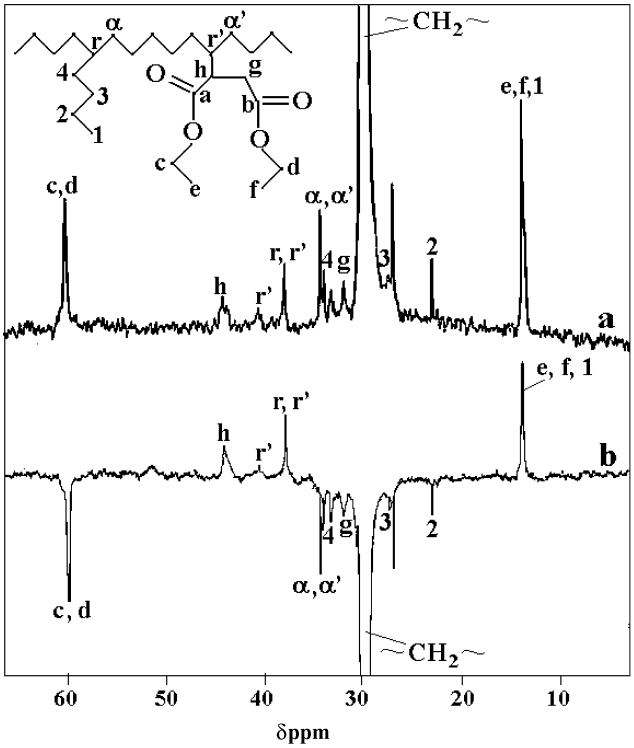

Fig. 8. ^{13}C NMR spectra of HDPE1-*g*-DEM: (a) ^{13}C NMR spectrum and (b) ^{13}C NMR-DEPT 135° spectrum.

allows the study of the variation of the signals corresponding to CH, CH_2 and CH_3 groups with the grafting. This technique facilitated the precise assignment of the signals, since in a DEPT 135° experiment the bands corresponding to the CH_2 groups were presented with negative phase, and those corresponding to CH and CH_3 groups with positive phase. An example of a ^{13}C NMR-DEPT 135° spectrum is given in Fig. 8(b) for HDPE1-*g*-DEM along with the corresponding band assignments (Fig. 8(a) shows the normal ^{13}C NMR spectrum for comparison purposes).

A very important result obtained in this work with the ^{13}C NMR-DEPT technique is that no quaternary carbons were detected after functionalization for any of the commercial polyethylene copolymers or even for the HPB which has the highest amount of branching amongst all the polymers under study (14 mol%, see Table 1). This result was deduced by comparing the ^{13}C NMR-DEPT 135° spectra for the functionalized polymers with the corresponding conventional ^{13}C NMR spectra and noticing that no signals disappear on going from the normal mode to the DEPT mode as shown in the example provided in Fig. 8(a) and (b) upon comparing the two spectra for HDPE1-*g*-DEM [42].

The only way to interpret this novel result in a satisfactory way is by considering that the grafting of DEM occurred mainly in secondary carbons and not in tertiary carbons as some authors have claimed in the past [21,22,29–31]. On the other hand, our results are in agreement with the report of Márquez et al. [18], who in order to explain their thermal fractionation results by SSA postulated that only a radical attack of DEM onto secondary carbons was consistent with a reduction of crystallizable linear sequences in the PE chains. As a matter of fact we have also performed SSA experiments that confirm these previous findings and the results will be presented below.

In the case of those samples with unsaturated vinyl groups at chain ends, it was shown above (Fig. 7) that some grafting can also occur in those sites until they are depleted. Nevertheless in the HPB case, where no unsaturations are present, the only grafting site according to our ^{13}C NMR-DEPT results are the secondary carbons since branching points are apparently not significantly affected by functionalization with DEM. The reason behind this lack of attack onto in principle more reactive tertiary carbons may be a combination of their relative lower numbers as compared to secondary carbons in the chains and also steric factors since the DEM molecule is rather large (additional evidences of steric effects are given below in Figs. 9 and 10).

The effect of the amount of chain branching present in the polyethylene was found to affect the exact position of the grafted DEM with respect to the branch point. In other words, the mean distance of the grafted DEM molecule from the nearest tertiary carbon was a function of the branching content but also of the functionalization degree.

Fig. 9 shows a ^{13}C NMR-DEPT 135° spectrum corresponding to HDPE2-*g*-DEM. We can identify the signals corresponding to the tertiary carbons in the main chain where the DEM is grafted, whose position varies with its relative distance to the neighboring tertiary carbon where the branch point is located. Along with the spectrum, Fig. 9 also present two possible chemical structures that correspond to a detailed signal analysis of the spectrum, note the labels in important carbon atoms. The two signals that are most prominent in the spectrum are those corresponding to carbons r and h. The position of grafted DEM has been deduced to be either in a β position with

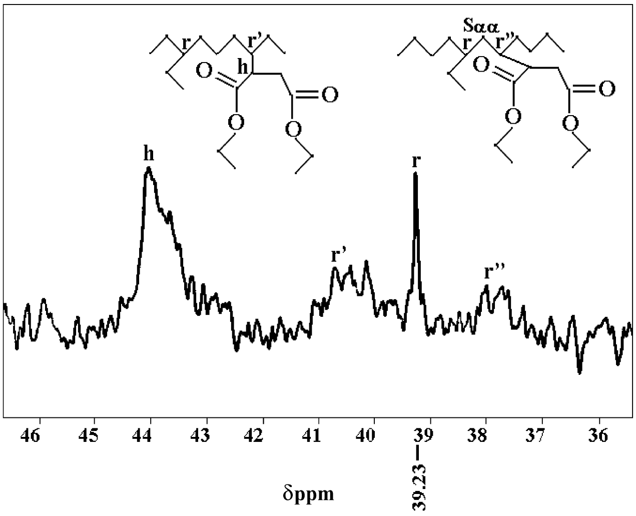

Fig. 9. ^{13}C NMR-DEPT 135° spectrum of HDPE2-*g*-DEM.

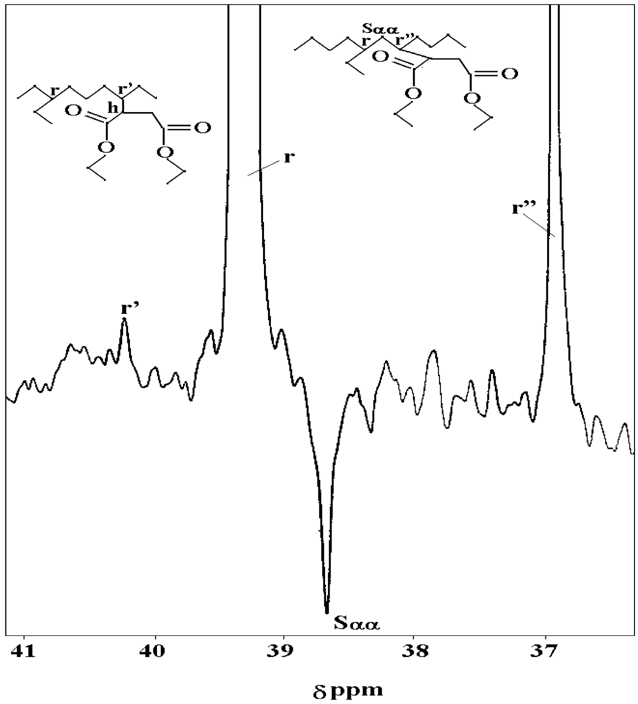

Fig. 10. ^{13}C NMR-DEPT 135° spectrum of HPB-*g*-DEM.

respect to the branching point (attached to carbons labeled r″) or located at a distance of 5 carbon atoms or more from the branching points (attached to carbons labeled r′). The signals corresponding to r″ and r′ can be distinguished since the distance between these carbon atoms and carbon r varies from 3 carbon atoms to 5 or more carbon atoms, respectively.

The presence of negative phase signals at around 38.6 ppm in Fig. 9 was expected in view of the above discussed DEM insertion at position r″. Such signals would correspond to secondary carbons in α position to both the olefinic branch and the grafted DEM (labeled $S_{\alpha\alpha}$ in the chemical structure inserted in the upper right hand corner of Fig. 9). According to the absence of such $S_{\alpha\alpha}$ signals in Fig. 9, it is reasonable to conclude that at least for HDPE2-*g*-DEM, the preferred grafting sites in secondary carbons are those located further away from the olefin branching points. The effect may again be related to a steric effect due to the voluminous structure of the DEM molecule. However, when the amount of chain branching is greatly increased, like in the sample of HPB used in this work, then the probability of grafting very close to the olefin branching point must increase.

Fig. 10 shows the ^{13}C NMR-DEPT 135° spectrum of the HPB-*g*-DEM. Two important bands are now very clear as compared to Fig. 9 for HDPE-*g*-DEM, they are the signal corresponding to r″ tertiary carbons and that corresponding to the $S_{\alpha\alpha}$ secondary carbons. It therefore seems likely that when a great number of branches are present in polyethylene, the DEM molecule can be grafted very close to the branching points.

The results presented in this section show that DEM insertion onto polyethylene chains preferentially occurs in secondary carbons of the main chain regardless of the branch type and content of the copolymer. The reason for this behavior may be related to steric effects produced by the size of the DEM molecules. It seems that DEM not only avoids the tertiary carbons where the branches are located but also, in polyethylene copolymers with less than 4 mol% branch content, it prefers to insert in the secondary carbons that are a few carbon atoms away from the branch point. A statistical factor is also involved since there is an excess of secondary carbons as compared to tertiary ones per PE chain that would explain why the peroxide attacks secondary carbons preferentially instead of more reactive tertiary ones. In those cases where unsaturations are present in PE chain ends, FTIR showed that they can also be depleted, presumably because of the characteristic steric freedom around these free ends besides the double bond reactivity.

3.2. Characterization by SSA

SSA is a thermal fractionation procedure [34–39] that is based on selecting chains with similar length of linear crystallizable sequences in view of their similar crystallization conditions, since the branches are normally excluded from the crystallization front. In the case of SSA the procedure differs from traditional thermal fractionation techniques that are based on sequential isothermal crystallization steps at decreasing temperatures [43] by the introduction of successive self-nucleation and annealing steps, where each cycle is similar to those designed by Fillon et al. [44] to study self-nucleation by DSC experiments.

Fig. 11 presents the final melting scans at 10 °C/min after applying the SSA technique to HPB before and after grafting with DEM. A series of melting endotherms can be seen in each DSC scan indicating that thermal fractionation was possible in these polymers. The method allows a separation of several fractions by short chain branching

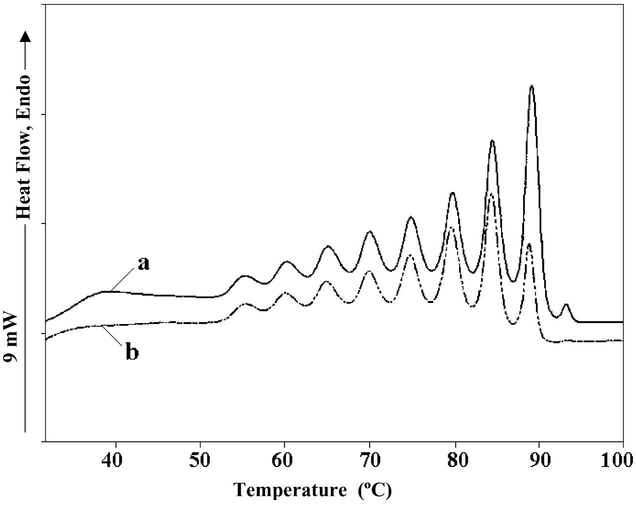

Fig. 11. Final heating scan after SSA for: (a) HPB and (b) HPB-*g*-DEM.

Table 3
Peak heights obtained for the most linear thermal fractions after SSA of selected materials

	Heights of the endotherms (mW[a])		
	Fraction 1	Fraction 2	Fraction 3
HDPE1	30.0	10.0	5.0
HDPE1-*g*-DEM	0	23.1	8.7
HPB	0.6	8.8	5.5
HPB-*g*-DEM	0.0	3.6	5.0
LLDPE3	23.0	4.0	5.0
LLDPE3-*g*-DEM	13.2	15.1	6.5

[a] The weight of the samples was always in the range 9.7–10 mg.

content, each fraction melts at a different temperature revealing a distribution of lamellar thickness that corresponds to the distribution of short chain branching (SCB) in the polymer under study. In the case of the neat HPB, the nine peaks located at temperatures from 55 to 95 °C correspond to the nine thermal fractions that were expected from the fractionation procedure applied. The lowest melting broad peak at approximately 40 °C corresponds to the melting of the crystals formed during cooling from the last T_s temperature applied. The melting point of each fraction is a function of the mean lamellar thickness formed during the SSA treatment and is directly proportional to the mean chain length between branching points. Therefore, the distribution of melting points observed in Fig. 11 can be transformed into a distribution of SCB if a calibration curve is available. Such calibration curves can be constructed by the use of preparative temperature rising elution fractionation (TREF) fractionation and subsequent analysis of the fractions by ^{13}C NMR [34,35,45–47].

Fig. 11 shows that HPB has a wide distribution of SCB. We will refer to the fractions by numbers starting from the highest temperature. The first fraction corresponds to that where the most linear chains within the distribution melt (i.e. that located at 93.2 °C) and it is a very small fraction as judged by its area. The most abundant fraction is fraction 2 since this is the one with the highest peak and the largest area (see below and Tables 3 and 4).

After grafting with DEM, HPB suffers an important change in its distribution of SCB. According to the SSA final scan shown in Fig. 11 for HPB-*g*-DEM the most linear fraction or fraction 1 has been completely lost, while a major reduction in fraction 2 leaves fraction 3 as the most abundant one. These changes are consistent with DEM insertion onto secondary carbons, thereby shortening the linear sequences available for producing thicker crystals.

The reduction in height and width at mid height of the endotherms corresponding to the 3 most linear fractions of HPB-*g*-DEM as compared to the unmodified HPB is shown in Table 3 and in Table 4. In this case the functionalization reaction causes a reduction of both height and width of most fractions without the increase of any of the fractions with higher branch contents. This is probably related to the fact that HPB already has a high amount of chain branching.

Table 4
Width at mid height obtained for the most linear thermal fractions after SSA of selected materials

	Width at mid height of the endotherms (°C)		
	Fraction 1	Fraction 2	Fraction 3
HDPE1	5.1	2.5	2.8
HDPE1-*g*-DEM	0.0	3.6	2.9
HPB	1.0	1.7	1.8
HPB-*g*-DEM	0.0	1.0	1.7
LLDPE3	2.7	2.4	2.2
LLDPE3-*g*-DEM	1.5	2.5	2.1

Fig. 12 shows the final melting scans after SSA for HDPE1 before and after functionalization. In this case, the most linear fraction is also the most abundant, a typical case of a copolymer with rather low branching content. After grafting with DEM, as in the HPB case, fraction number 1 was completely depleted. However, in this case it is very clear that fractions 2–5 increase in height and area. Tables 3 and 4 show how fractions 2 and 3 increase their value of height and width while fraction 1 disappears after grafting. This result indicates that once the linear sequences that use to be part of fraction 1 were interrupted by the grafted DEM, their length is reduced and they are able to crystallize at lower temperatures and therefore take part of a fraction with a higher SCB content (i.e. fractions 2 or higher number).

An intermediate behavior between that observed for HPB and that for HDPE1 was found after SSA with LLDPE3, as shown in Fig. 13 and Tables 3 and 4. In this case, the most linear fraction is not completely depleted after grafting with DEM but it is substantially reduced while fractions 2–4 increase in height and area.

The above presented results and similar previous analysis [18] indicate that grafting reactions with DEM are occurring

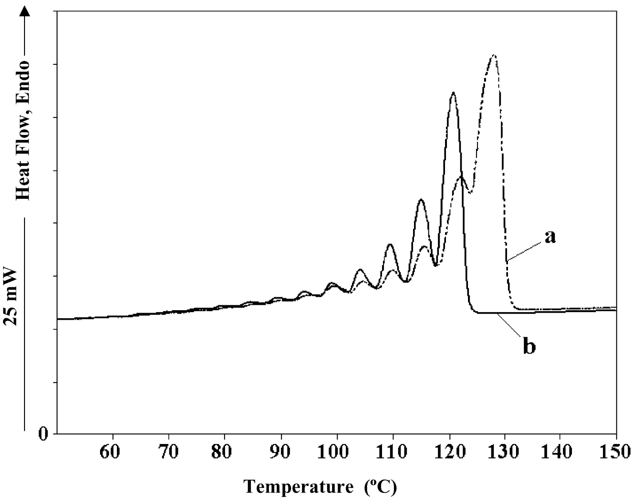

Fig. 12. Final heating scan after SSA for: (a) HDPE1 and (b) HDPE1-*g*-DEM.

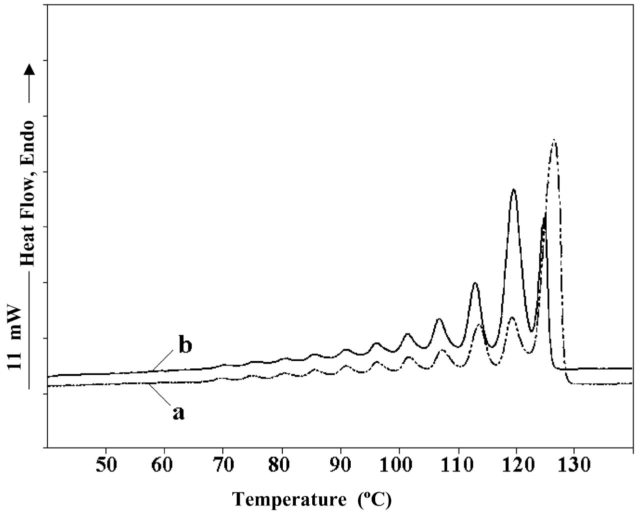

Fig. 13. Final heating scan after SSA for: (a) HDPE3 and (b) HDPE3-*g*-DEM.

preferentially for these polyolefins in the secondary carbons within the main chain, even when FTIR results indicated that DEM grafting at the beginning of the reaction can proceed by radical attacks on the terminal unsaturations [19].

3.3. Proposed mechanism for polyethylene grafting with DEM

From the results obtained by FTIR, NMR and SSA the products after DEM grafting onto PE chains have been identified and, as indicated above, DEM insertion occurs predominantly onto secondary carbons. A tentative mechanism is presented in Fig. 14 that is consonant with the reaction products obtained, however, other routes to obtain DEM insertion onto secondary carbons should not be ruled out.

The primary radicals generated by the thermal decomposition of DBPH are shown in Fig. 14 to abstract secondary hydrogen atoms from PE chains forming macroradicals. Tertiary radicals may also form but because our results indicated a lack of DEM insertion in such sites, we decided not to depict this possibility in Fig. 14 on the assumption that a statistical process could favor the formation of secondary radicals since the chain branching content is relatively low. The grafting reaction is derived from these macroradicals by an attack on DEM molecules.

Previous analysis [14] obtained by NMR demonstrated that the functionalization occurs by isolated units of DEM, without detecting oligomers of DEM, either linked to the chain or homopolymerized.

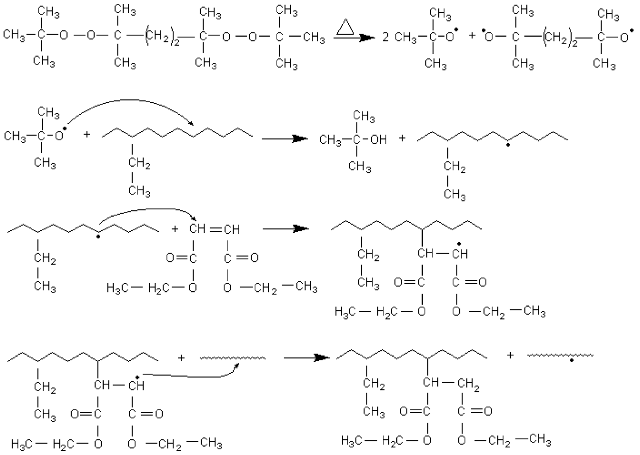

Fig. 14. Proposed grafting mechanism for HDPE.

4. Conclusions

The obtained results indicate that the grafting with DEM occurs in different places of the chain: at the beginning of the reaction, it may proceed by insertion on terminal unsaturations if they are present in the chain, then the grafting reactions occur preferentially in the secondary carbons within the main chain. Results by NMR evidenced that although tertiary carbons are more reactive than secondary ones, the grafting does not occur in these sites. The reason for this behavior may be related to two effects: first, a statistical factor could provoke the production of a higher number of secondary radicals since there is an excess of secondary carbons as compared to tertiary ones per PE chain; second, steric effects may be produced by the size of the DEM molecules. Our ^{13}C NMR-DEPT results suggest that DEM not only avoids the tertiary carbons where the branches are located but also, in polyethylene copolymers with less than 4 mol% branch content, it prefers to insert in the secondary carbons that are at least 5 carbon atoms away from the branch point. The thermal fractionation performed by SSA corroborated the results mentioned above since the fractions with the longest linear sequences were always the first to be depleted by the grafting reactions.

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